

A Synergistic Approach to the Development of New Hydrogen Storage Materials

A. Paul Alivisatos, Marvin L. Cohen, Jean M. J. Fréchet,
Martin Head-Gordon, Jeffrey R. Long, Steven G. Louie, Samuel S. Mao,
Thomas J. Richardson, and Alex Zettl

*Departments of Chemistry and Physics, University of California, Berkeley
and Divisions of Materials Science and Environmental Energy Technologies,
Lawrence Berkeley National Laboratory*

May 19, 2006

OVERALL VISION

- Bring together a group of scientists with a broad range of perspectives and experiences in materials discovery, and get them thinking about and working on the problem of hydrogen storage
- Utilize theory as much as possible in guiding experiments
- Ensure that the exchange of new ideas and results is facile
- Ensure that the instrumentation for measuring hydrogen storage is immediately accessible to the primary researchers—this **WILL** be the rate-limiting step in discovering new materials

PROGRAM OVERVIEW

Synthesis and characterization of metal/metal hydride nanocrystals (Alivisatos)

Synthesis and characterization of nanostructured boron nitrides (Zettl)

Theory predictions for nanostructured boron nitrides (Cohen and Louie)

Set-up of H₂ storage characterization instrumentation at LBNL (Mao)

Synthesis and characterization of microporous polymers (Fréchet)

Synthesis and characterization of microporous coordination solids (Long)

First-principles determination of H₂ binding energies (Head-Gordon)

Synthesis and characterization of destabilized hydrides (Richardson)



9/05
start

BES



EERE

12/04
start



H₂ STORAGE CHARACTERIZATION INSTRUMENTS (Mao)



Hiden Isochema IGA

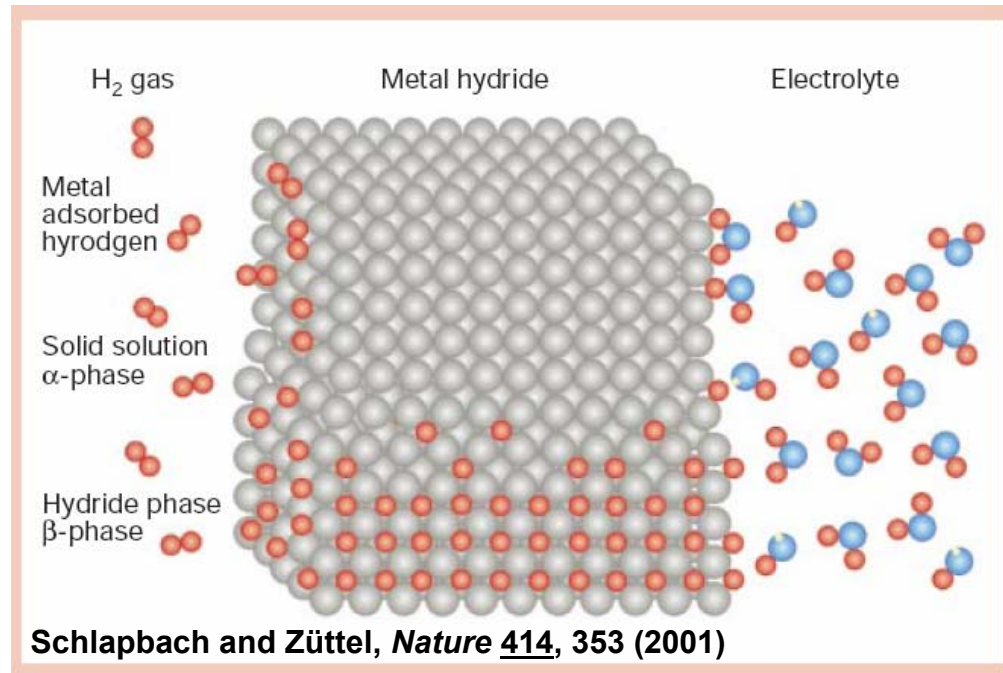
installed 7/05



Hy-Energy PCTPro-2000

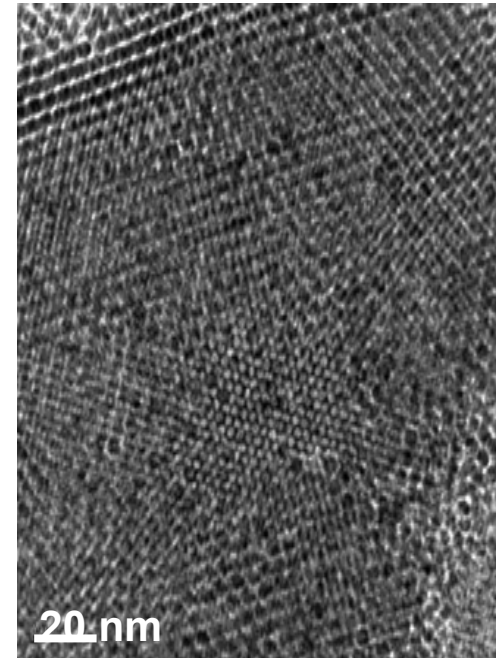
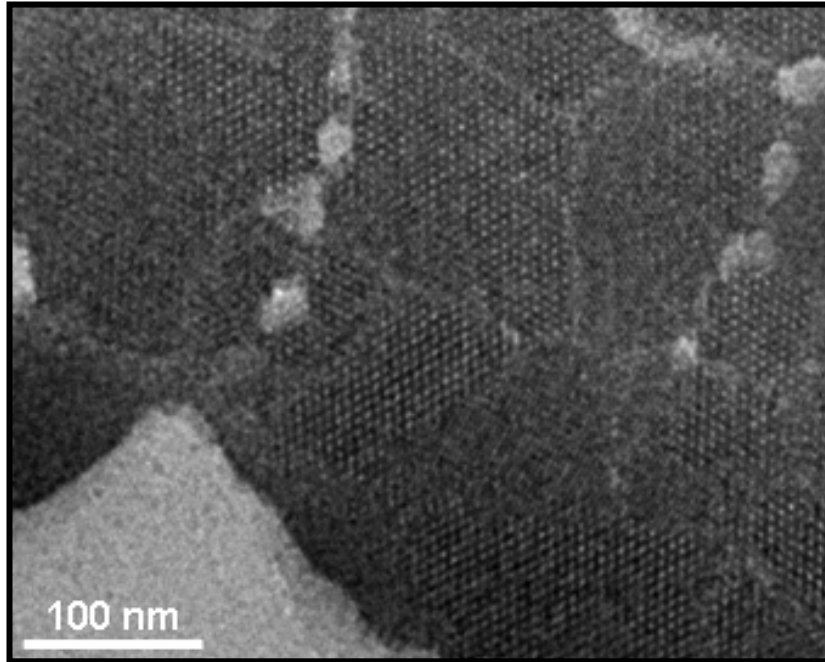
delivery expected 7/06

H₂ UPTAKE IN METAL NANOCRYSTALS (Alivisatos)



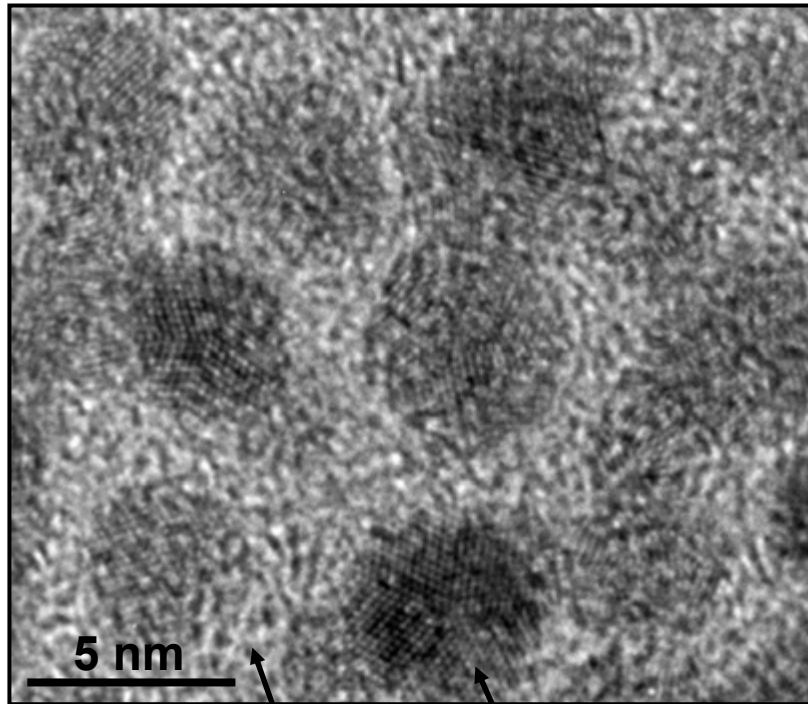
- High surface area to volume ratio can alter kinetics and maybe thermodynamics
- Study effects of manipulating nanocrystal size, shape, and capping ligands
- Start with well-understood Pd system and move to lighter metals (e.g., Mg, Al)

3-D SUPERLATTICES OF 5-nm Pd NANOCRYSTALS



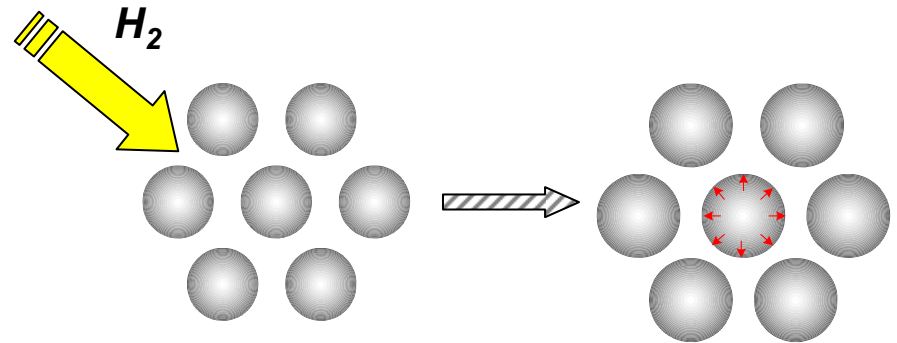
- Superlattices may reduce strain, combating embrittlement and hysteresis
- Goal is to monitor nanocrystal shape and volume during H₂ uptake and release
- Then optimize system by adjusting nanocrystal size and interparticle spacing

CHARACTERIZATION OF H₂ ADSORPTION IN 3-D ARRAYS



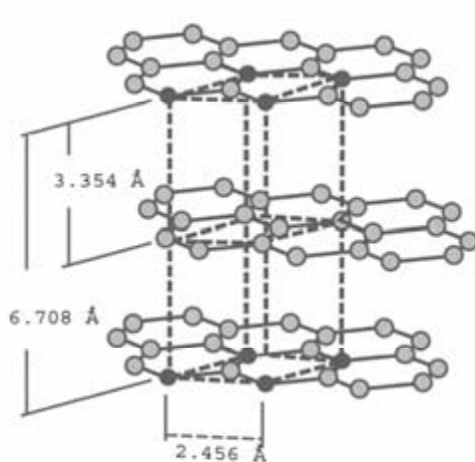
soft, organic shell

inorganic core

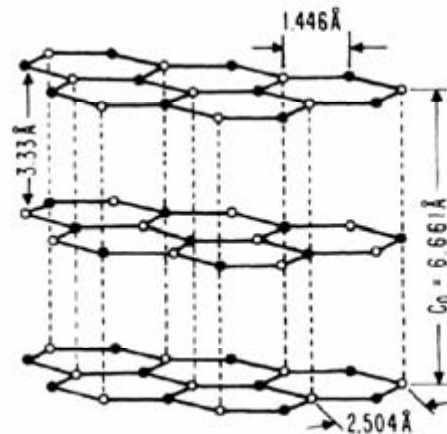


- *In situ* X-ray diffraction and TEM
- Pressure-composition isotherms
- Thermogravimetric analysis
- X-ray photoelectron spectroscopy

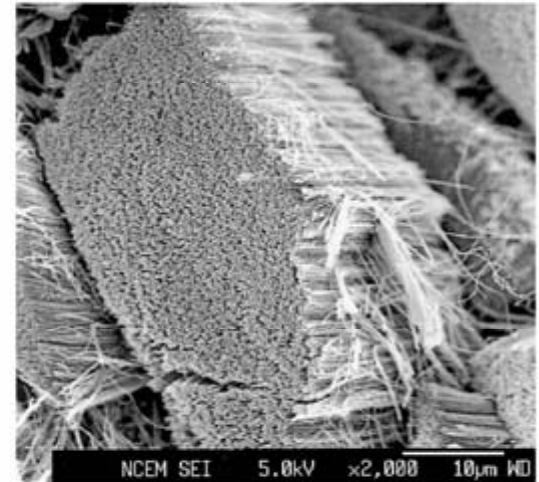
SYNTHESIS OF NANOSTRUCTURED BORON NITRIDE (Zettl)



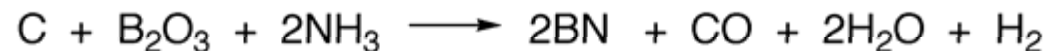
graphite



BN

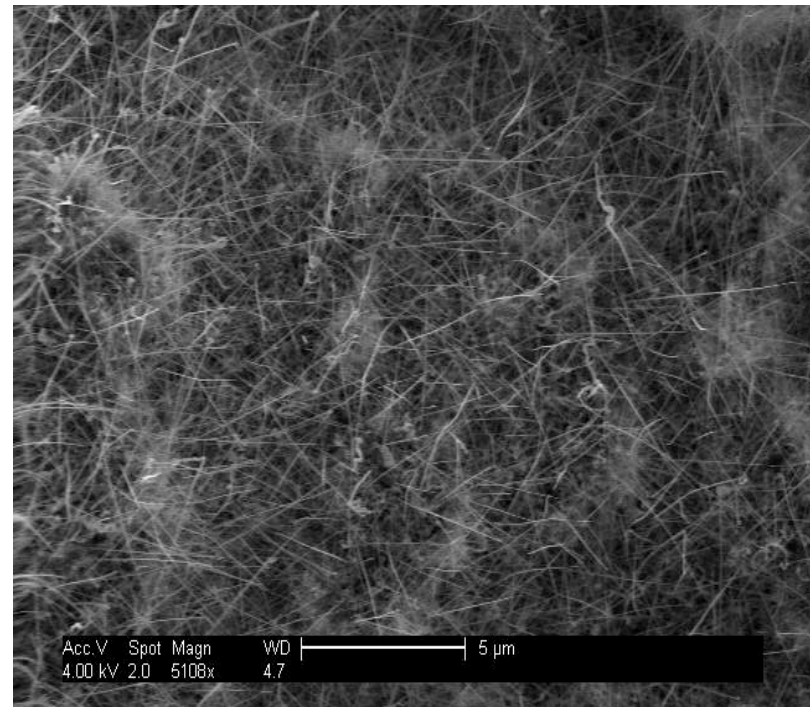
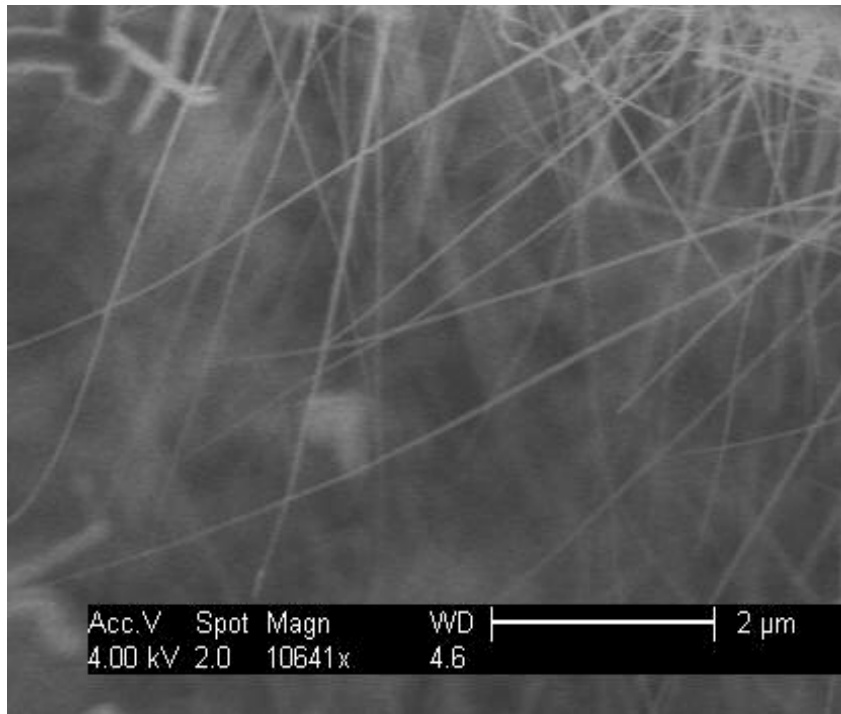


- Zettl group has discovered a CVD-like method by which carbon nanotubes can be converted directly into BN nanotubes:



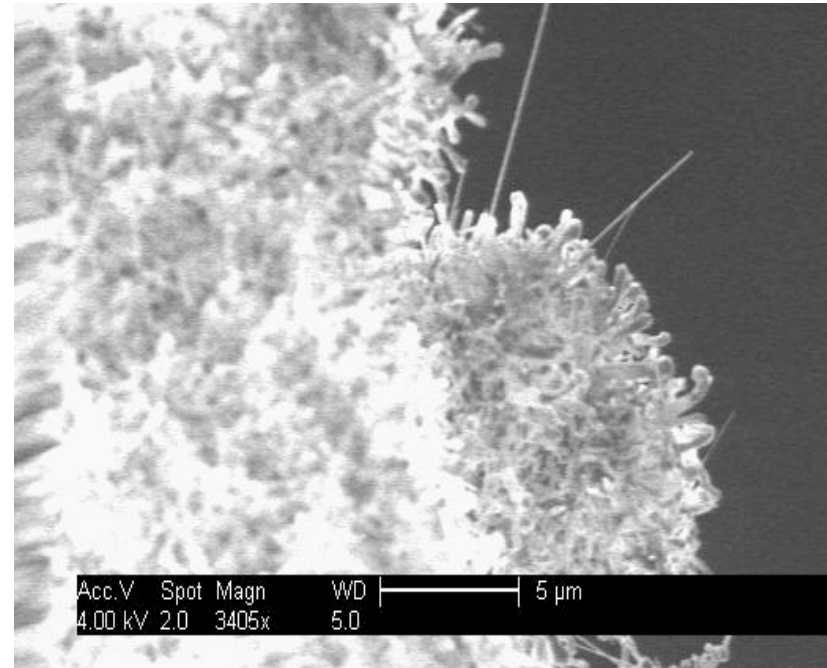
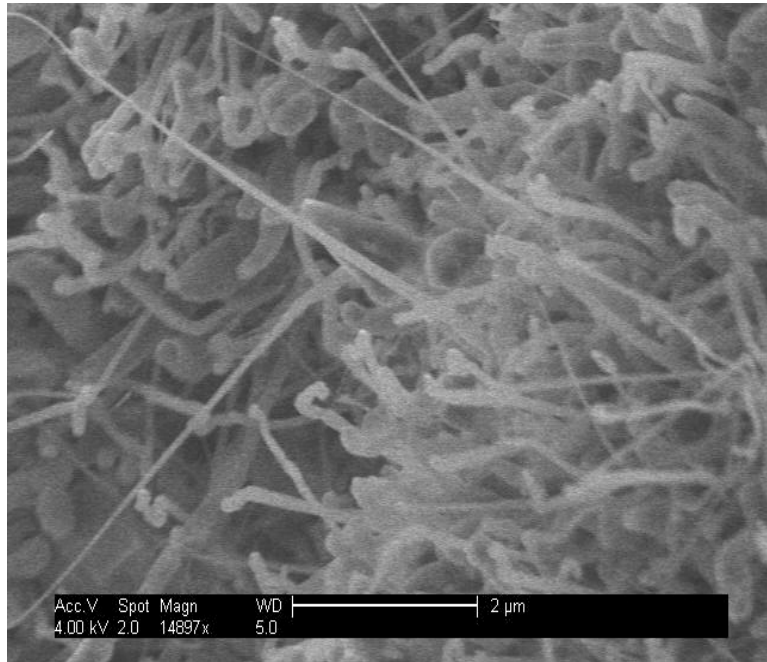
- Approach will be applied in converting other forms of carbon into nanostructured BN
- Intermediate materials of the type $\text{C}_x\text{B}_y\text{N}_z$ will also be investigated

LARGE-SCALE PRODUCTION OF PURE BN NANOTUBES



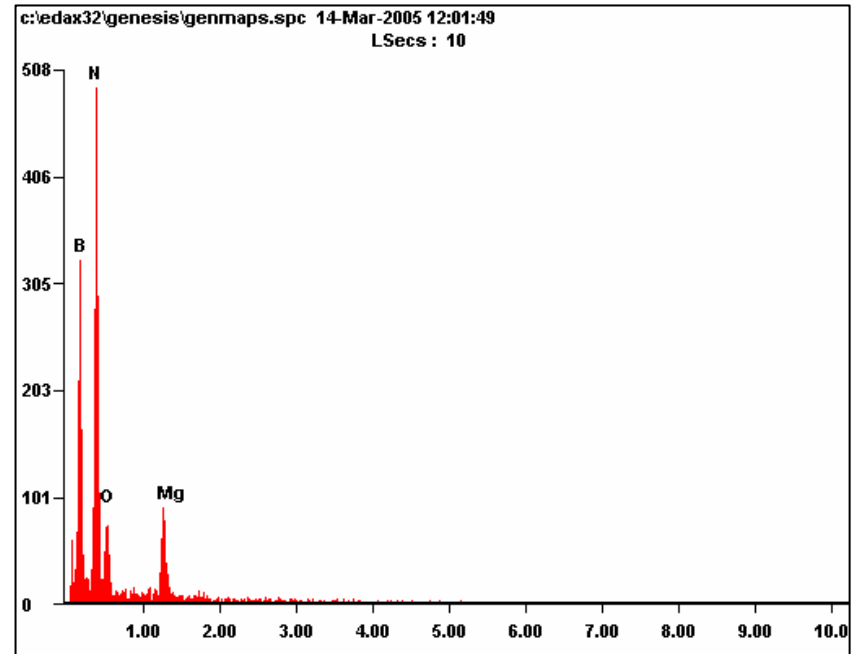
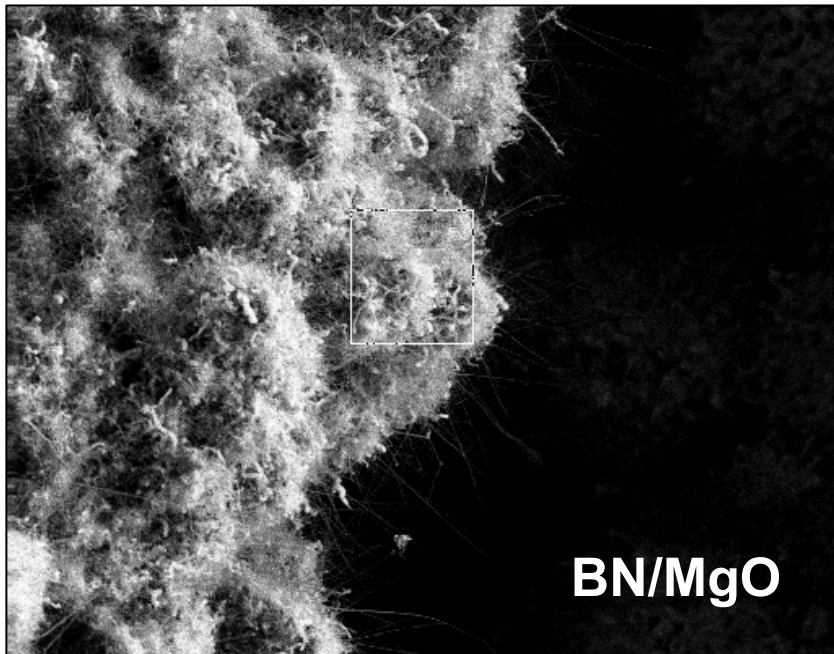
- Both CVD and induction furnace methods have been refined

VARYING THE MORPHOLOGY OF BN NANOPARTICLES



- Initial form of the carbon nanostructure can be used to adjust BN morphology
- Gas sorption measurements underway to compare surface areas and H₂ storage

SYNTHESIS OF BN-NANOPARTICLE COMPOSITES



- CVD methods also being developed to produce composites with metal and metal oxide nanoparticles

COMPUTATIONAL METHODS FOR BN SOLIDS

(Cohen and Louie)

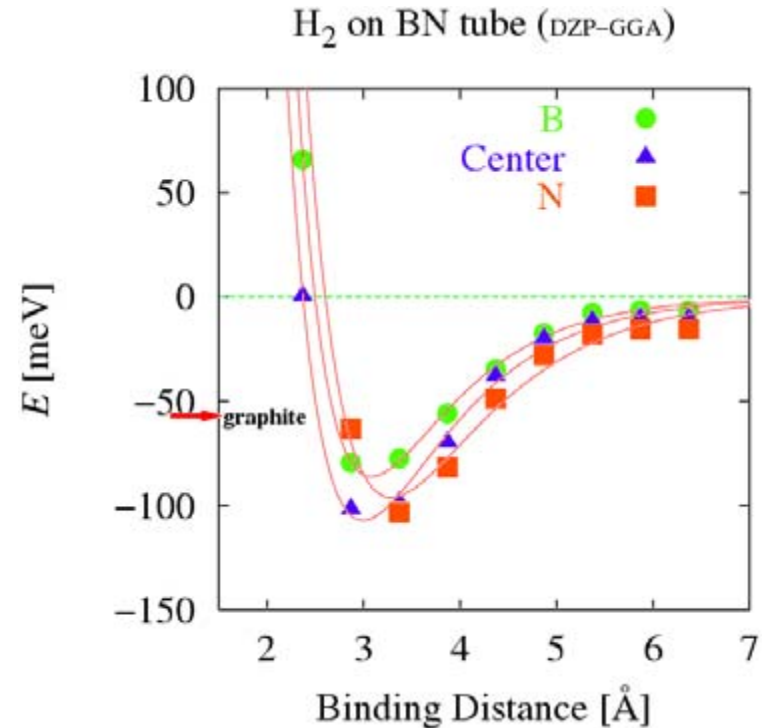
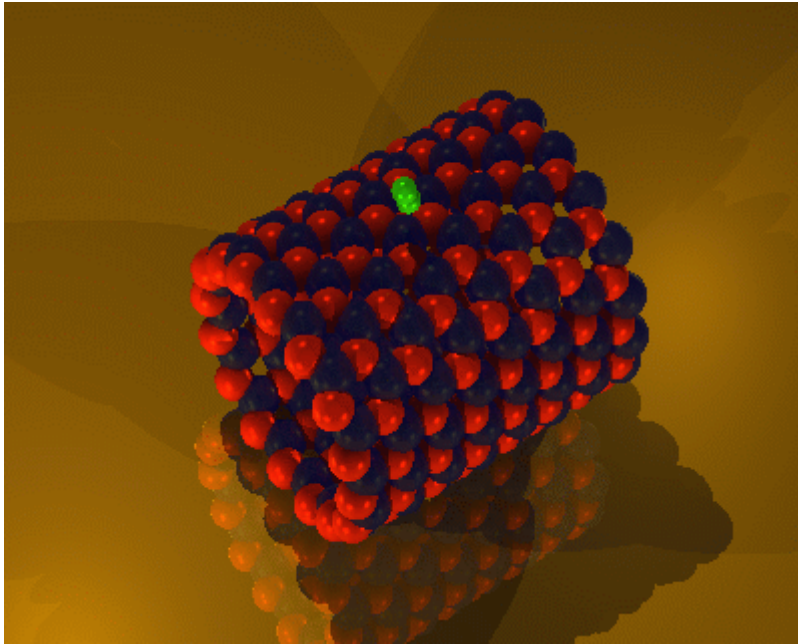
Ab initio density functional theory for H₂ binding energy calculations:

- Pseudopotential method; basis = atomic orbitals/planewaves
- Exchange-correlation $V_{e-e}[\rho]$: generalized gradient approximation (GGA)
- Variation principle to $E[\rho]$
- One-particle Schrödinger equation: $[-\nabla^2 + v(r) + V_H(r) + V_{XC}(r)]\psi(r) = \varepsilon\psi(r)$

Adsorption theory for calculating H₂ storage capacities:

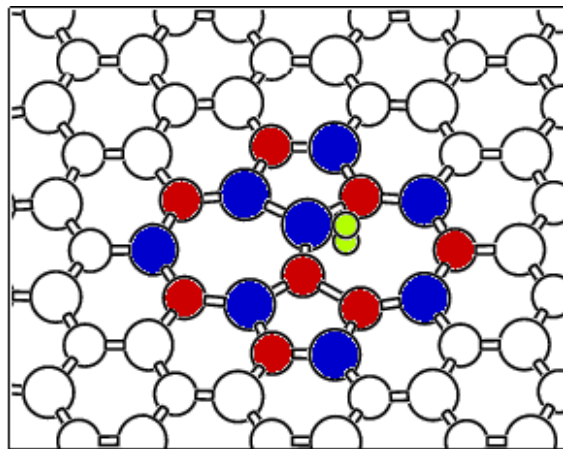
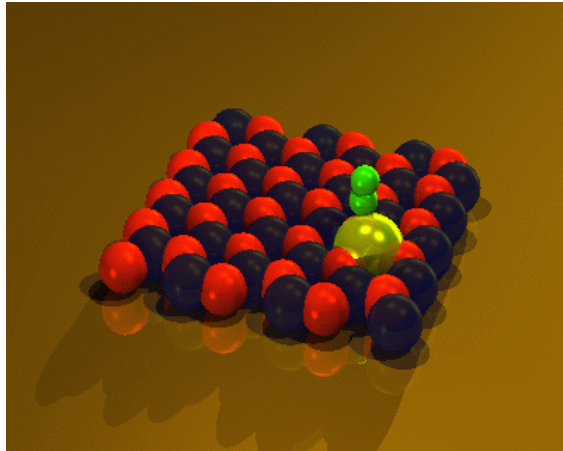
- van't Hoff equation: $\ln p_0 = -\Delta H/kT + \Delta S/R$
- Langmuir isotherms: $\theta = \frac{p/p_0}{1 + p/p_0}$

H₂ ADSORPTION ON BN NANOTUBES

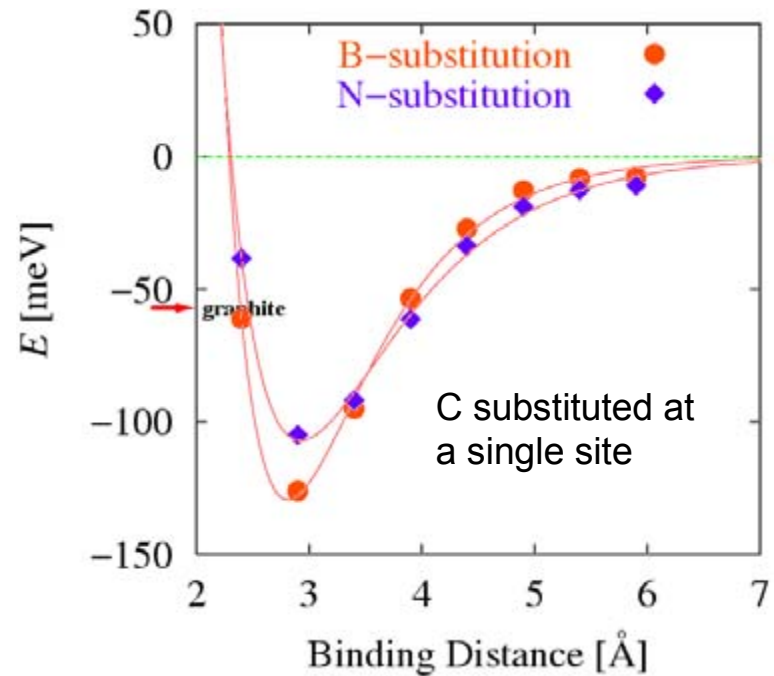


- Strongest binding sites are over N atoms and above ring centers
- Enhanced binding of 10 kJ/mol compared with ~7 kJ/mol for carbon tubes

H₂ ADSORPTION AT DEFECT SITES IN BN NANOTUBES

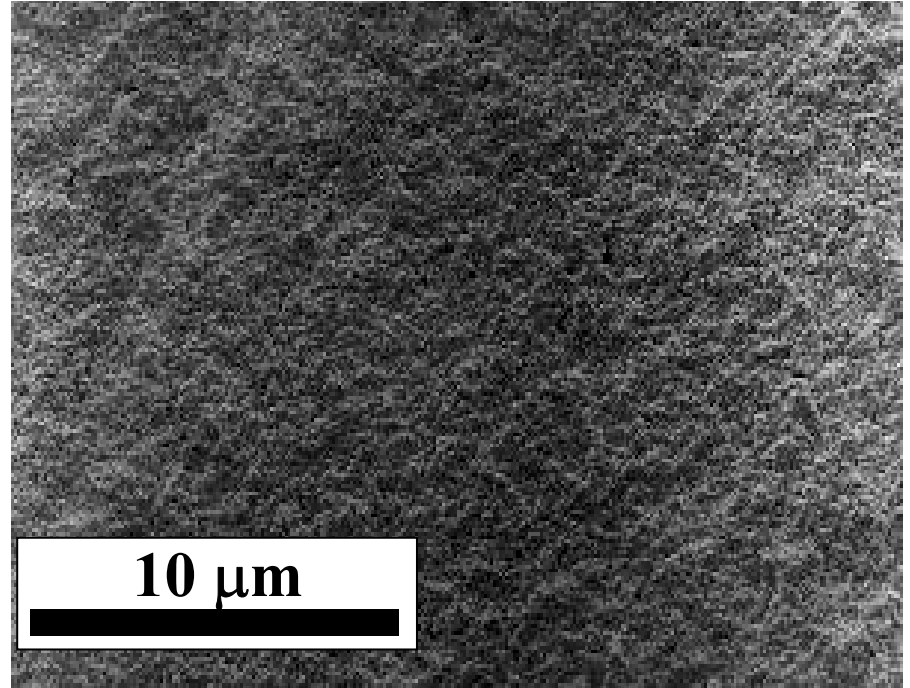
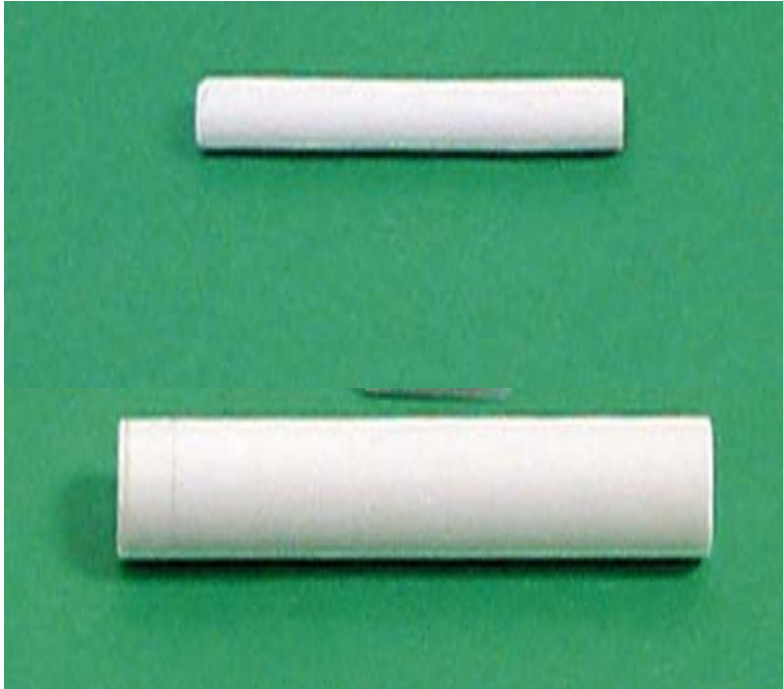


Stone-Wales defect



- Binding energies increase by 10-30% relative to perfect tubes

MICROPOROUS POLYMERS (Fréchet)

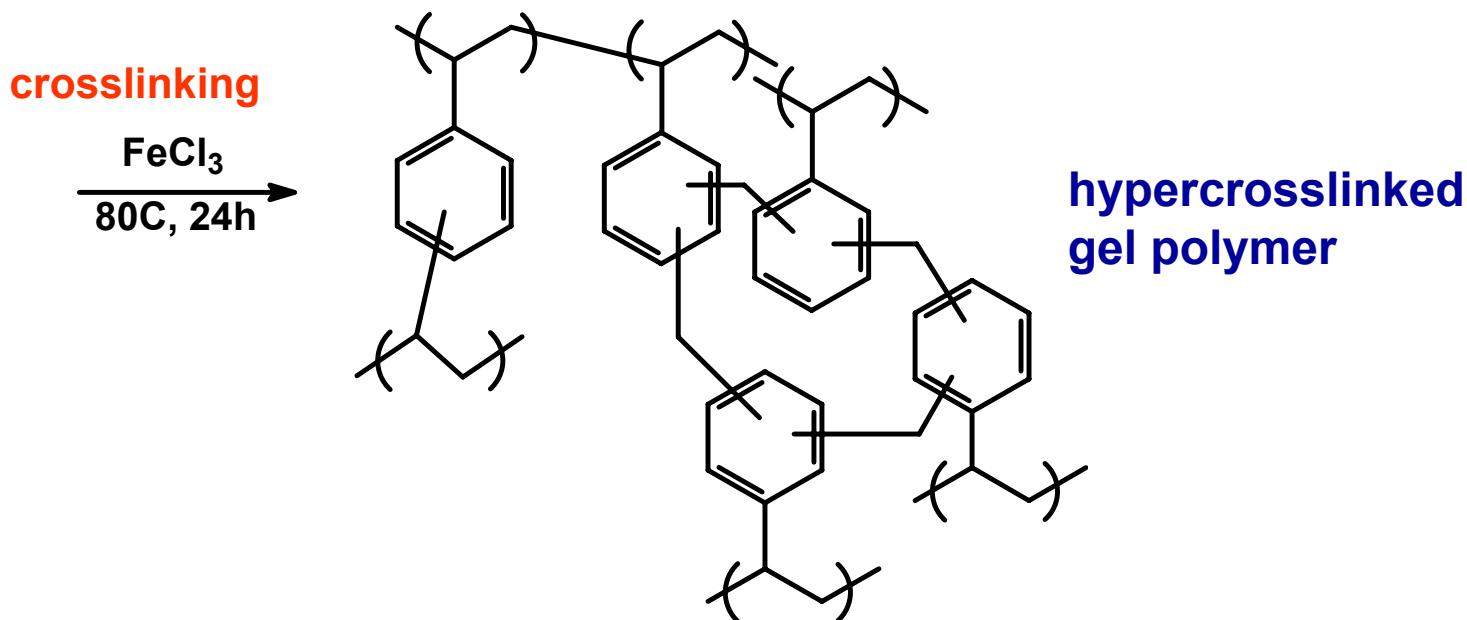
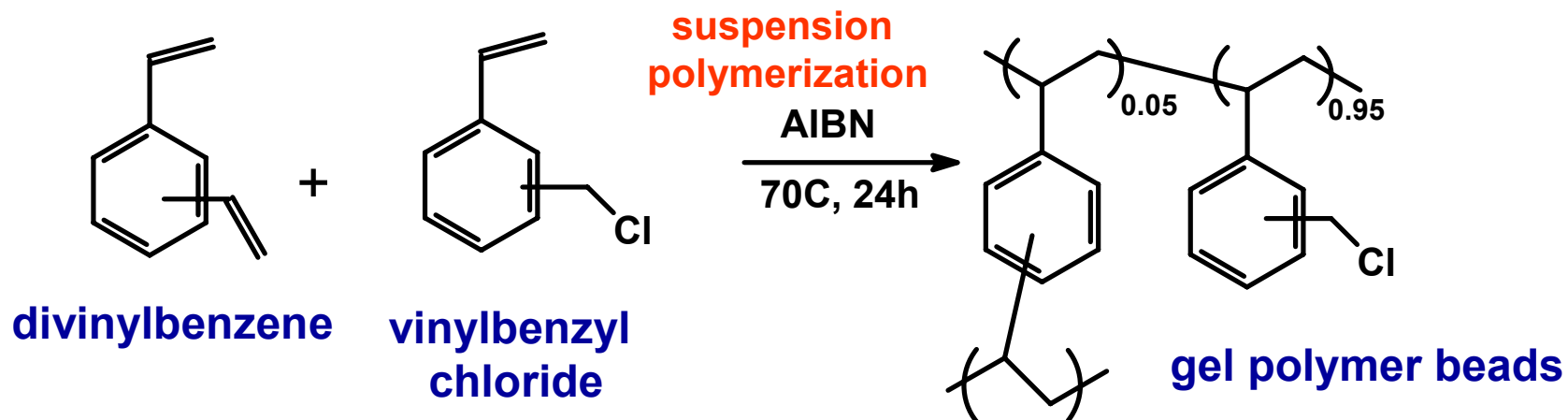


- Generally inexpensive materials that can be produced on a large scale
- Readily processed: can be molded to produce monoliths of any shape and size
- Surface characteristics can be tuned using well-established molecular chemistry

GAS SORPTION IN POROUS FORMS OF COMMERCIAL RESINS

Trade name	Composition	BET surface area (m ² /g)	H ₂ capacity at 77 K and 1 bar (wt%)
Amberlite XAD4	poly(styrene-co-divinylbenzene)	1,060	0.8
Amberlite XAD16	crosslinked aliphatic polymer	770	0.6
Lewatit EP63	poly(styrene-co-divinylbenzene)	1,200	1.3
Haysep N	poly(divinylbenzene-co-ethylene dimethacrylate)	460	0.5
Hypersol-Macronet MN200	hypercrosslinked polystyrene	840	1.3

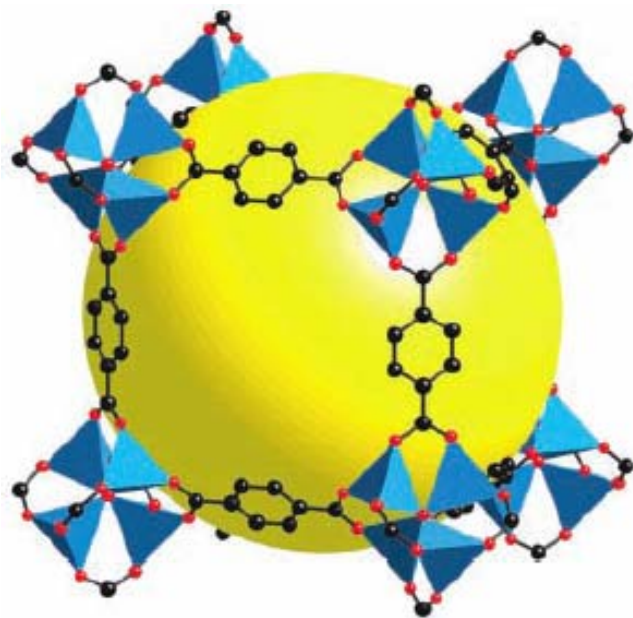
SYNTHESIS OF HYPERCROSSLINKED POLYMERS



GAS SORPTION IN HYPERCROSSLINKED POLYMERS

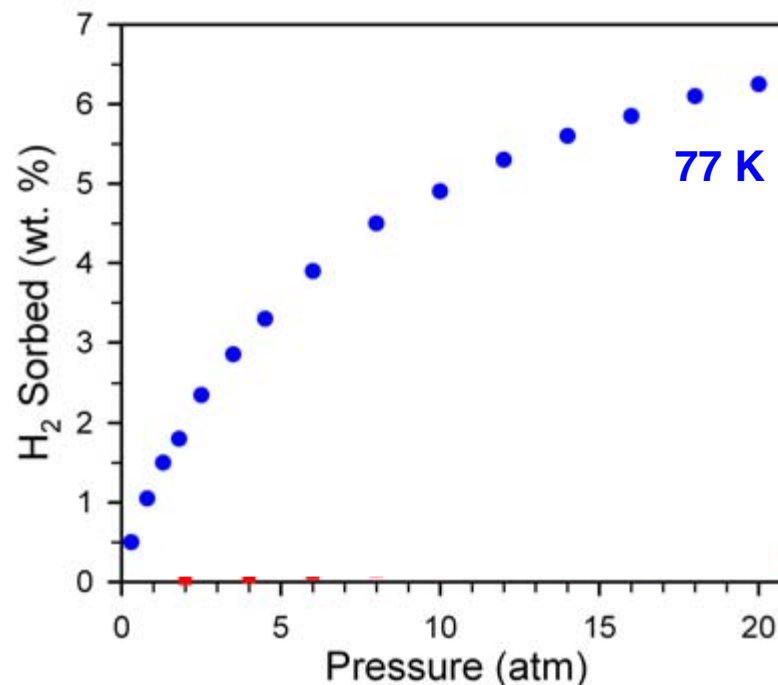
Precursor	Composition (%)	Character	BET surface area (m ² /g)	H ₂ capacity at 77 K and 1 bar (wt%)
Poly(vinylbenzyl chloride -co- divinylbenzene)	40.0 : 60.0	macroporous	310	0.4
		↓ hypercrosslinked polymer	1,300	1.20
Poly(vinylbenzyl chloride -co- divinylbenzene)	2.5 : 97.5	gel	0	0
		↓ hypercrosslinked polymer	1,930	1.55

MICROPOROUS COORDINATION SOLIDS (Long)



$\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$

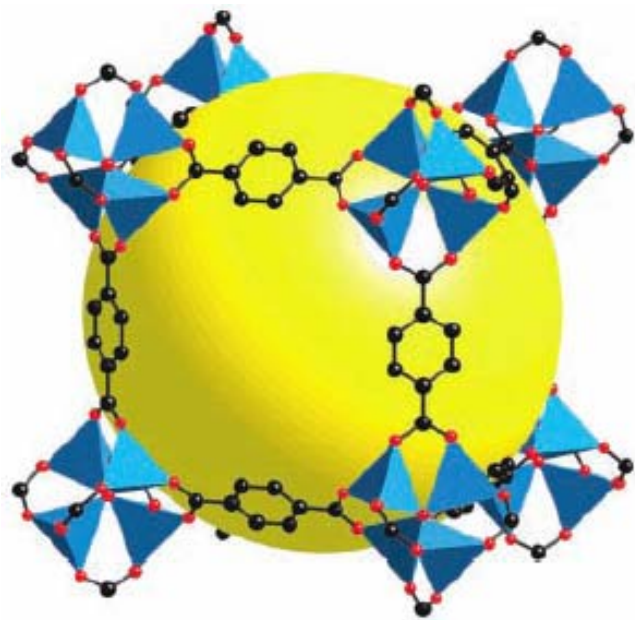
Yaghi and coworkers



Our results agree with Yaghi's

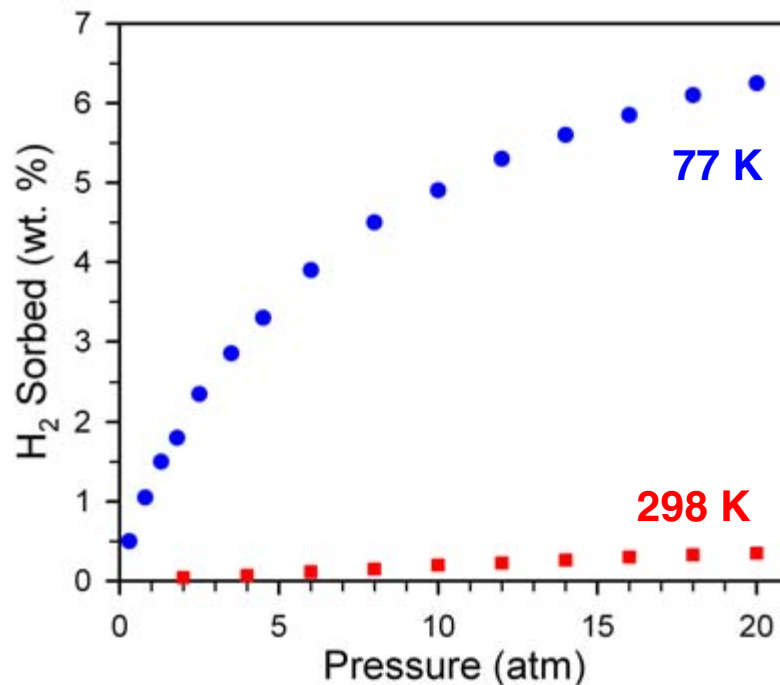
- Gravimetric storage capacity is quite high
- No strong binding sites, leads to adsorption enthalpy of just 5 kJ/mol
- Our goal is to create materials of this type with exposed metal coordination sites

MICROPOROUS COORDINATION SOLIDS (Long)



$\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$

Yaghi and coworkers



Our results agree with Yaghi's

- Gravimetric storage capacity is quite high, but only at low temperature
- No strong binding sites, leads to adsorption enthalpy of just 5 kJ/mol
- Our goal is to create materials of this type with exposed metal coordination sites

H₂ BINDING ENTHALPIES



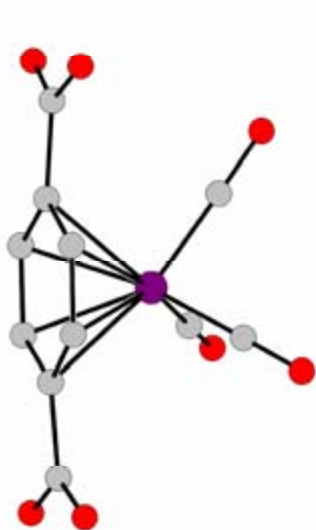
- Wide variation in binding enthalpy, depending upon character of metal and surrounding ligands
- For a storage material that operates at room temperature and moderate pressures would like to achieve:

$$\Delta H = 10\text{-}20 \text{ kJ/mol}$$

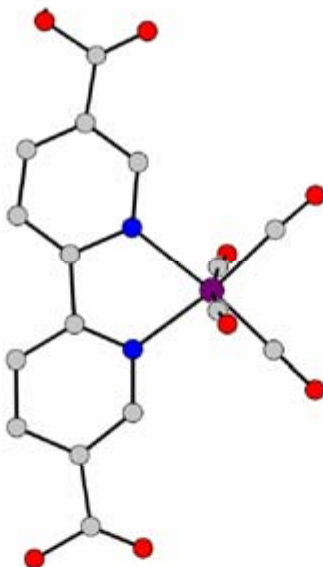
- Target lightweight metal ions that can potentially sustain many exposed coordination sites

M	ΔH (kJ/mol)
Li ⁺ _(g)	27
Na ⁺ _(g)	10
K ⁺ _(g)	6
Ti ⁺ _(g)	37
Cu ⁺ in chabazite	56
CuCl surface	93
Cr(CO) ₅	78
Mo(CO) ₅	81
Cr(CO) ₃ (PCy ₃) ₃	31
Mo(CO) ₃ (PCy ₃) ₃	27
W(CO) ₃ (PCy ₃) ₃	42
OsH ₂ (CO)(P ⁱ Pr ₃) ₂	82

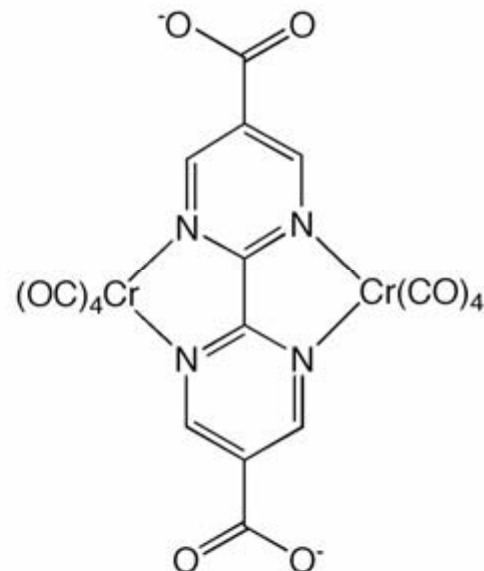
INCORPORATING METAL BINDING SITES



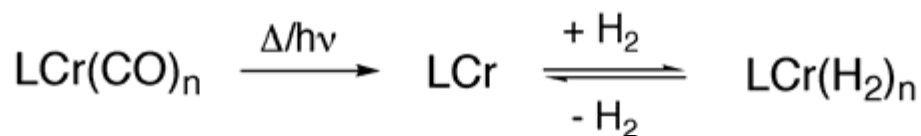
2.8 %



4.2 %

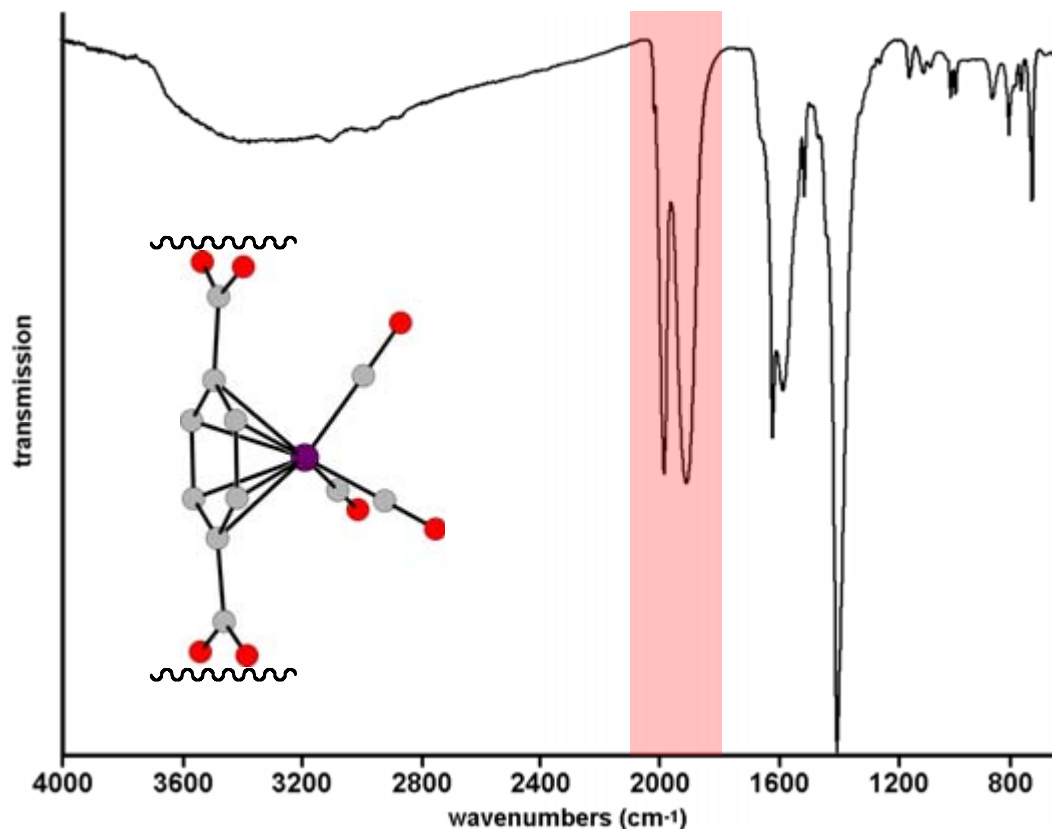
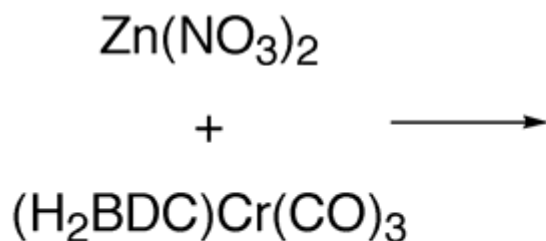


6.1 %



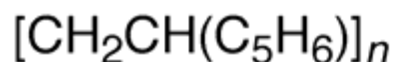
- Rigid framework will pin coordinatively-unsaturated metal centers, preventing aggregation
- Adjust binding affinity by varying metal center and/or ligand substituents

SYNTHESIS OF $\text{Zn}_4\text{O}(\text{BDC-Cr}(\text{CO})_3)_3$

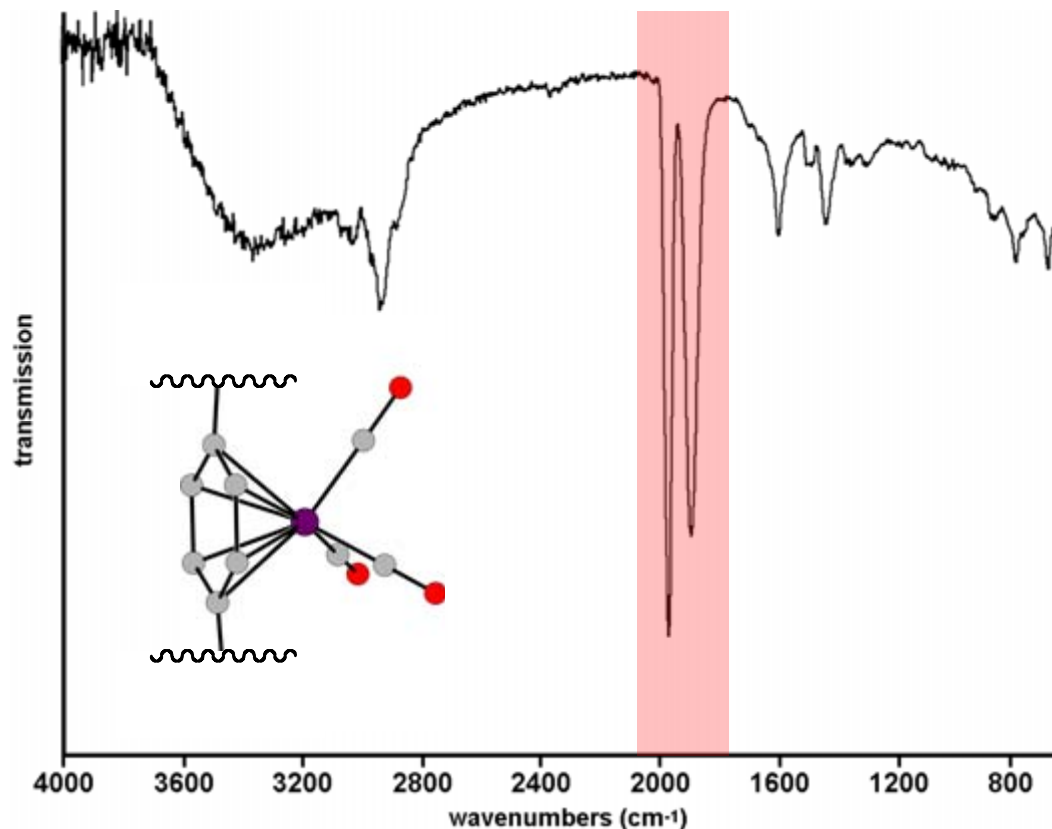
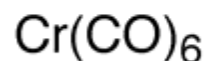


- Dark orange-red solid with the usual cubic structure by powder X-ray diffraction
- Intense CO stretches in IR spectrum are very similar to those of molecular precursor

METALLATION OF A MICROPOROUS POLYMER

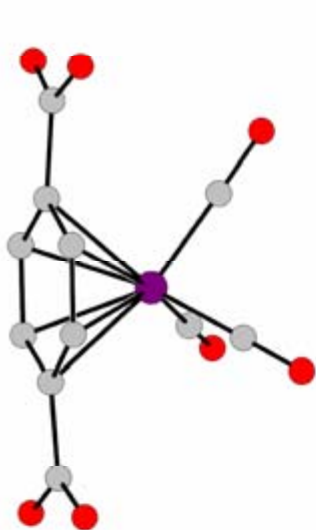


+

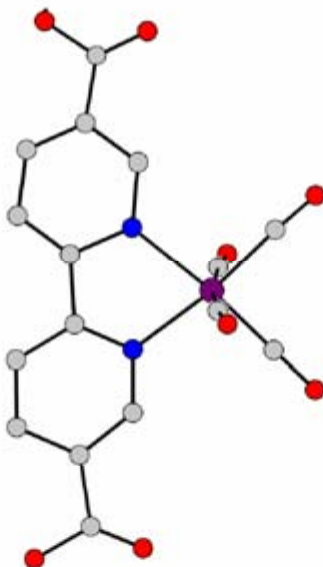


- Polymer turns dark orange-red in color and BET surface area drops to 650 m²/g
- Appearance of CO stretches and comparison with model complex indicate incorporation

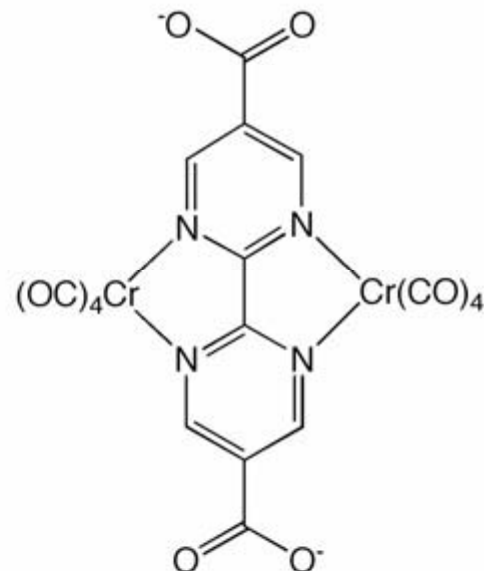
INCORPORATING METAL BINDING SITES



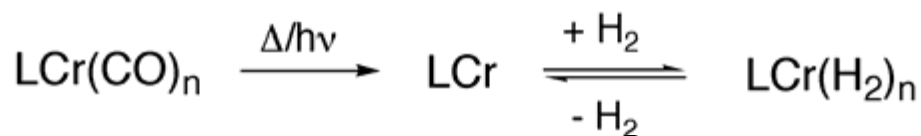
2.8 %



4.2 %

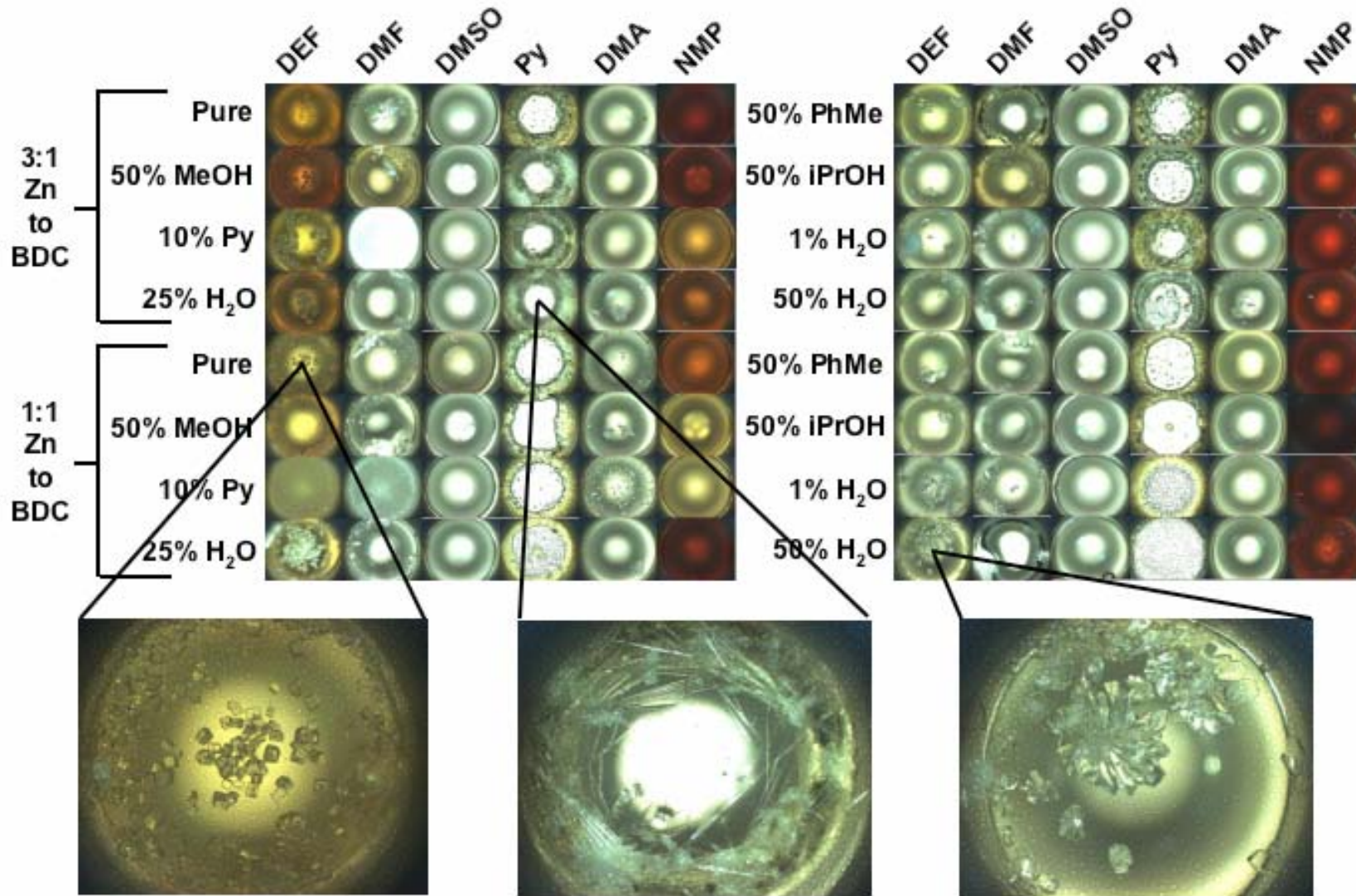


6.1 %



- Rigid framework will pin coordinatively-unsaturated metal centers, preventing aggregation
- Adjust binding affinity by varying metal center and/or ligand substituents

HIGH THROUGHPUT FRAMEWORK SYNTHESIS



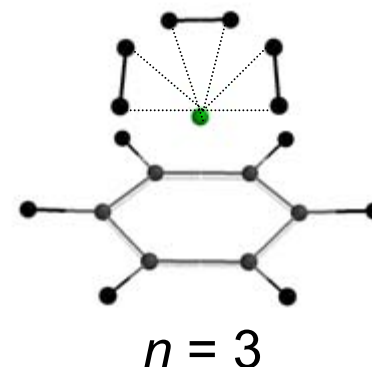
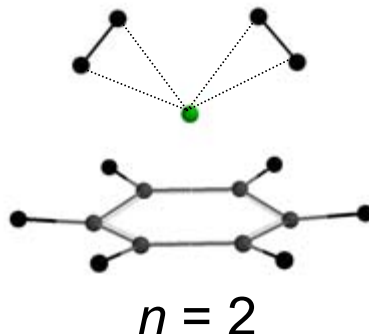
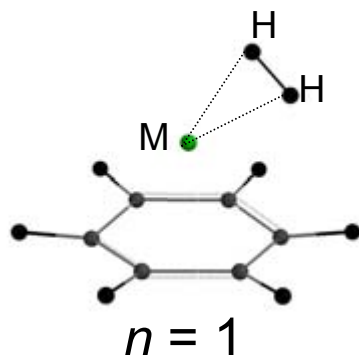
with Tom Boussie and Dawn Verdugo at Symyx Technologies

CALCULATION OF H₂ BINDING AFFINITIES (Head-Gordon)

- **Goal:** Apply first-principles electronic structure calculations to evaluate interactions of H₂ with ligands and metals employed in microporous polymers and coordination solids
- Theory must accurately assess a range of possible effects:
 - Dispersion interactions (weak)
 - Interactions with localized charges (charge-quadrupole interactions)
 - Charge-transfer interactions involving forward and/or back donation
- Technical details:
 - Use our own optimized code (Q-Chem)
 - Use MP2 theory to correctly describe dispersion interactions (unlike DFT)
 - Use auxiliary basis expansions and local methods for efficiency
 - Correct energies for basis set superposition error

H₂ BINDING TO METAL-BENZENE COMPLEXES

BP86/SRSC/6-311G** results for (C₆H₆)M(H₂)_n complexes:

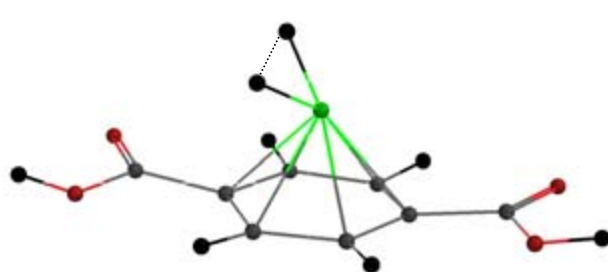


M = Cr	D_0 :	16.0 kcal/mol	12.9 kcal/mol	12.5 kcal/mol
	H-H:	0.906 Å	0.868 Å	0.888 Å
M = Mo	D_0 :	25.1 kcal/mol	13.4 kcal/mol	15.8 kcal/mol
	H-H:	1.525 Å	0.895 Å	0.915 Å

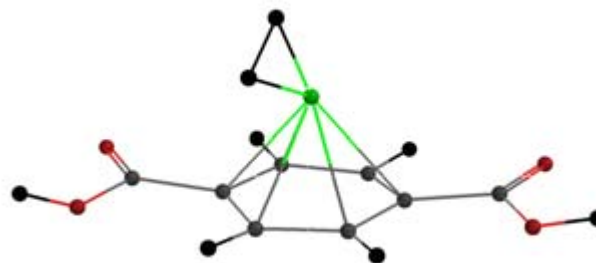
- Binding energies are a factor of 4 larger than desired
- Calculations on other first-row transition metals are in progress

H₂ BINDING TO METAL-H₂BDC COMPLEXES

BP86/SRSC/6-311G** results for (H₂BDC)M(H₂)_n complexes:



M = Cr

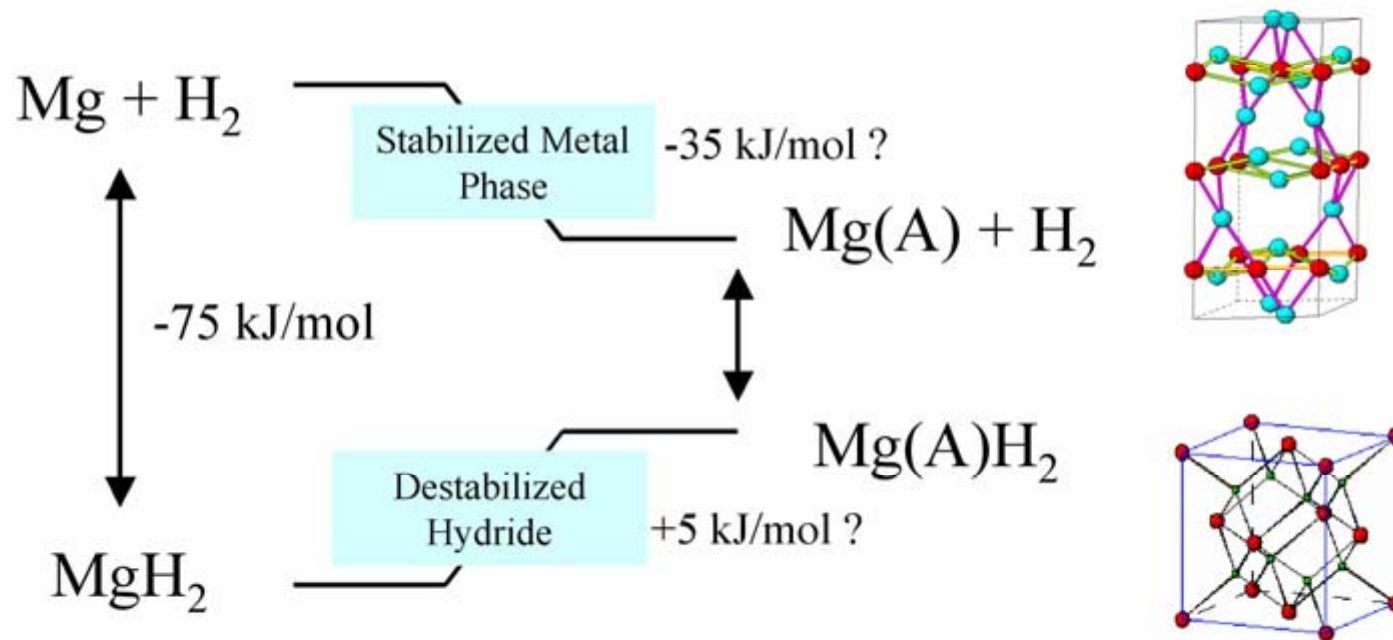


M = Mo

D_0 :	14.8 kcal/mol	22.6 kcal/mol
H-H:	0.885 Å	1.013 Å

- Carboxylic acid substituents lower binding energy by ~2 kcal/mol
- Calculations will study effects of utilizing other benzene substituents

STABILIZED LIGHT METAL ALLOYS (Richardson)



- Research in the Richardson lab has already demonstrated destabilization of MgH_2 by doping with a few atom percent of a transition metal element
- Stabilization of the magnesium alloy can likely provide a larger energy change
- Both transition and main group metals are under investigation for this purpose

ACKNOWLEDGMENTS

Graduate Students

Mircea Dinca
Steven Kaye
Peter Liska
Rohini Lochan
Jonathan Germain

Undergraduates

Marcus Gibson
Alina Siu
Charlene Tsay
Anta Yu

Postdoctoral Fellows

Dr. Hye Jin Choi
Dr. Kelly Flook
Dr. Won Seok Han
Dr. Rachel Smith

Staff Scientists

Dr. Elena Shevchenko
Dr. Frantisek Svec

Collaborators

At NIST:
Dr. Craig Brown
Dr. Michael Hartman
Dr. Yun Liu
Dr. Dan Neumann
Dr. Vanessa Peterson
At Symyx:
Dr. Tom Boussie
Dr. Dawn Verdugo

Funding

DOE
UC Berkeley